Evaluation of the efficiency of an experimental biocover to reduce BTEX emissions from landfill biogas

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Abstract:

Landfill emissions include volatile organic compounds (VOCs) and, particularly, benzene, toluene, ethyl-benzene and xylene isomers (collectively called BTEX). The latter are the most common VOCs found in landfill biogas. BTEX affect air quality and may be harmful to human health. In conjunction with a study aiming to evaluate the efficiency of passive methane oxidizing biocovers, a complementary project was developed with the specific goal of evaluating the reduction in VOC emissions due to the installation of a biocover. One of the biocovers constructed at the Saint-Nicéphore (Quebec, Canada) landfill site was instrumented for this purpose. The total BTEX concentration in the raw biogas ranged from 28.7 to 65.4 ppmv, and the measured concentration of BTEX in biogas emitted through the biocover ranged from below the limit of detection (BLD) to 2.1 ppmv. The other volatile organic compounds (OVOC) concentration varied from 18.8 to 40.4 ppmv and from 0.8 to 1.2 ppmv in the raw biogas and in the emitted biogas, respectively. The results obtained showed that the biocover effectiveness ranged from 67 to 100% and from 96 to 97% for BTEX and OVOC, respectively.

Key words: biogas, biocover efficiency, landfill, volatile organic compounds

1. Introduction

Landfill biogas (LFG) is produced under anaerobic conditions by the biodegradation of the waste materials (Chiriac et al., 2007). The composition of LFG varies significantly both spatially and temporally but generally includes 40 to 45 vol% CO_2, 55 to 65 vol% CH_4, and minor quantities of organic alcohols, aromatic hydrocarbons, halogenated compounds, sulfur compounds, etc. LFG typically includes numerous volatile organic compounds (VOCs) (Durmusoglu et al., 2010; Rasi et al., 2011), which are formed in landfills as intermediary or final products of microbial or abiotic degradation processes (Chiriac et al., 2007; Rasi et al., 2011).

Common VOCs found in LFG are benzene, toluene, ethyl-benzene and xylene isomers (Durmusoglu et al., 2010), commonly referred as BTEX. The BTEX compounds form an important group of VOCs because of their deleterious effect on the tropospheric chemistry and due to their neurotoxic, carcinogenic and teratogenic properties (Allen et al., 1997; Durmusoglu et al., 2010). The VOC concentrations in LFG range from 0.2 to 4500 mg m^{-3} and their concentration range depends on the age, quantity, quality and origin of the waste - which can vary from one landfill cell to another, as well as on the climatic conditions prevailing in the area where the landfill is installed (Durmusoglu et al., 2010).

One promising biotechnology to attenuate landfill surface emissions is to install a biocover over the site (Hrad et al., 2012). Although a significant body of literature exists about the reduction of methane emissions from landfills with such technology (Scheutz et al., 2009), few studies (e.g. Scheutz et al., 2008; Durmusoglu et al., 2010) have focused on VOC removal by biocovers.

2. Materials and Methods

2.1. Description of the Experimental Passive Methane Oxidizing Biocovers

The experimental biocover (Fig. 1) was constructed in 2006 within an existing final cover of the Saint-Nicéphore (Quebec, Canada) landfill in an area where the waste mass was approximately 5 yr old. This biocover is 2.75 m wide, 9.75 m long and 1.2 m deep and is composed of the following layers, from bottom up: i) a 0.3 m layer of 12.7 mm clean gravel, whose role is to distribute the biogas as uniformly as possible; ii) a 0.1 m transitional layer of 6.4 mm gravel; and iii) a 0.8 m substrate layer. The substrate consisted of a mixture of five volumes of compost (before sieving through a 12 mm industrial sieve) and one volume of coarse sand. The biocover was fed to the gravel layer from a dedicated biogas well at a controlled flow rate. The biogas loading during the monitoring campaign was approximately 7 L min^{-1}.

2.2. Biogas sampling

Ten sampling campaigns took place from August 14, 2012 through September 10, 2012. For each sampling campaign, a 10 L sample of raw biogas was collected from a biogas collecting well into Tedlar bags (Fig. 2a). In order to collect the emitted biogas, a 260 L rectangular steel flux chamber was used (Fig. 2c). The flux chamber is 1.8 m (L), 1.2 m (W) with a height of 0.12 m. The chamber was mounted on a metal frame that was inserted to a depth of 0.1 m into the biocover (Fig. 2b). A peristaltic pump was used to collect 10 L samples from the flux chamber into the Tedlar bags. The peristaltic pump flux rate was adjusted to a value equal to the methane surface flux, which was measured as part of the activities of another on-going project.

2.3. Analytical equipment

A solid-phase micro-extraction (SPME) fibre (Carboxen/PDMS, 85 µm, Supelco, Bellefonte, PA, USA) was used to extract and concentrate VOCs from the biogas collected at Saint-Nicéphore landfill site. The SPME method has been frequently employed to identify VOCs from various sources (Davoli et al., 2003; Kleeberg et al., 2005; Capelli et al., 2012).

For the identification and the quantification of VOCs, a GC-MS (G1800A, Hewlett-Packard, Agilent Technologies, Mississauga, ON, Canada) equipped with an electron ionization detector and an HP-5 MS fused-silica column (30 m X 0.25 mm id., 0.25 mm film thickness, Hewlett-Packard, Agilent Technologies, Mississauga, ON, Canada) was used. The analyses were conducted in full-scan mode over an *m/z* range of 50 to 450 amu. Calibration curves were prepared from 5 concentrations for each BTEX compound, each time using triplicates. The detection limit was (in ppbv): 1.8, 38.1, 4.1 and 24.5 for benzene, toluene, ethyl-benzene and xylene, respectively. The total BTEX and the other volatile organic compound (OVOC) concentrations were expressed in terms of "toluene–equivalent" (Chiriac et al, 2011). The performances of the biocover were evaluated in terms of BTEX and OVOC removal efficiency (RE, %) and its associated elimination capacity (EC, g m^{-3} h^{-1}).

3. Results and discussions

The BTEX concentrations in the raw biogas ranged from below the limit of detection (BLD) to 21.9 ppmv (Table 1). Xylene exhibits the highest value, followed by toluene, and ethylbenzene. In the emitted biogas, the BTEX concentration is in the range of BLD to 1 ppmv (Table 1) and the highest value (1 ppmv) was obtained for toluene. Xylene and ethylbenzene concentrations varied within a narrow range of concentrations (0.5 to 0.7 ppmv). Benzene was not detected in either raw biogas or emitted biogas. In addition to BTEX compounds, OVOCs were quantified in the raw and in the emitted biogas. A summary of the OVOC concentrations is presented in Table 1. Over the sampling period, the OVOC concentrations ranged from 18.8 to 40.4 ppmv in the raw biogas, and from 0.8 to 1.2 ppmv in the emitted biogas. The total BTEX concentration ranged from 28.7 to 65.4 ppmv in the raw biogas, and from BLD to 2.1 ppmv in the emitted biogas.

Results of the RE to reduce VOC emissions are given in Table 2. The RE in reducing biogas emissions ranged from 67 to nearly 100% for BTEX, and from 96 to 97% for OVOCs. The associated EC ranged from 0.5 to 0.9, from 0.1 to 0.5 and from 0.7 to 1.2 mg m^{-3} h^{-1} for toluene, ethylbenzene and xylene, respectively. For OVOC, EC was in the range of 0.9 to 1.9 mg m^{-3} h^{-1}.

The high rates of RE to reduce VOC emissions obtained can be influenced by a number of factors such as: i) the moisture and the temperature in the biocover, ii) the soil pH (Lu et al., 2002), and iii) the organic nutrients available in the biocover soil (Lu et al., 2002). The organic matter content indicates the presence of nutrients for bacterial growth (e.g. Ait-Benichou et al., 2009). In our biocover, organic matter content equal to 20% $g_{o.m}/g_{dry\ soil}$. It was reported that a biofilter composed of natural packing materials like compost demonstrated better performance in VOC removal compared to soil amendment (Cho et al., 2009).

During the sampling period, the atmospheric temperature at the Saint-Nicéphore landfill site varied from 13 to 28 °C. Over the same period, the soil temperature at 10 cm in the biocover ranged from 30 to 35 °C. According to Cho et al. (2009) the suitable temperature to remove BTEX in biofiters ranged from 23 to 33 °C.

The BTEX biodegradation reaction is inhibited in acidic environments (Hunt et al., 1998). According to Lu et al (2002), biofilter efficiency to remove BTEX is greater than 80% when pH was in the range of 7.5 to 8. In this study, the pH value of the biocover was equal to 7.2 ± 0.1.

Over the sampling period, the degree of water saturation (S_r) of the biocover was measured at a depth of 10 cm and it was under 80%. These values are still lower than the value beyond which the air within the pores of the substrate become occluded (i.e. $Sr \sim 85\%$) (Nagaraj et al., 2006). According to He et al. (He et al., 2008) and to Ait-Benichou et al. (Ait-Benichou et al., 2009), the high values of the S_r of the biocover can be attributed to the water-retention capacity of the organic matter rich substrate (compost). When the value of S_r is below 13%, methanotrophic bacteria become inactive (Humer and Lechner, 1999).

4. Conclusions

Our results showed that the biocover installed on the landfill of Saint-Nicéphore is effective reducing VOC emissions into atmosphere. It can be concluded that the biocover represents an interesting biotechnology to reduce VOC emissions from landfill sites into the atmosphere. To facilitate a better understanding of biocover VOC removal efficiency from landfill sites, it would be of interest expanding our knowledge regarding: i) the methanotroph count at the vertical profiling of biocover; ii) estimation of RE at different vertical levels of the cover soil; iii) the vegetation effect on RE to reduce VOC emissions from landfill; and iv) the relationship between methane oxidation and VOC removal by the biocover.

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Figure captions

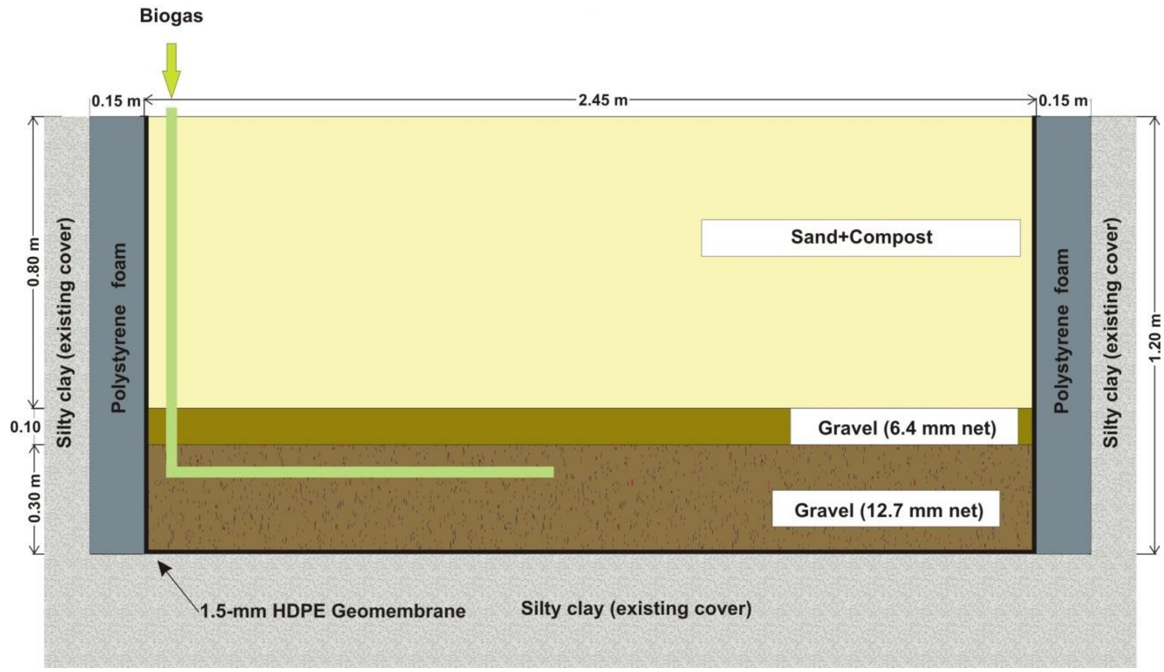

Fig. 1 Scheme of biocover installed in Saint-Nicephore site

Fig. 2 Equipment to collect raw and emitted biogas a) Tedlar bags, b) metal frame, and c) flux chamber

Table captions

Table1 VOC concentrations range in LFG during the sampling period

Compound	Raw biogas (ppmv)	Emitted biogas(ppmv)
Benzene	BLD[1]	BLD
Toluene	11.1 to 19.2	BLD to 1
Ethylbenzene	1.5 to 9.5	0.5 to 0.6
Xylene	13.3 to 21.9	0.6 to 0.7
C_{TBTEX}[2]	28.7 to 65.4	BLD to 2.1
C_{OVOCs}[3]	18.8 to 40.4	0.8 to 1.2

[1]= Below the limit of detection; [2]= Total BTEX concentration; [3]= Other volatile organic compoundsconcentrations; BTEX excluded.

Table 2 Efficiency and elimination capacity of the biocover

Compound	Biocover	
	EC* (mg m^{-3} h^{-1})	Efficiency (%)
Benzene	N.A.	N.A.
Toluene	0.5 to 0.9	95 to 100
Ethyl-benzene	~0.1 to 0.5	67 to 94
Xylene	0.7 to 1.2	95 to 97
OVOCs**	0.9 to 1.9	96 to 97

* = Elimination capacity;N. A. = Not applicable; ** = Other volatile organic compounds (BTEX excluded)